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Airborne inhalable metals in residential areas of Delhi, India: distribution, source apportionment and health risks

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ABSTRACT

The inhalable fraction of ambient particles (particulate matter with aerodynamic diameter less than 10 µm, denoted by PM_{10}) collected at three residential sites in Delhi, India during December 2008–November 2009 were characterized with respect to 8 major and trace metals (Fe, Mn, Cd, Cu, Ni, Pb, Zn and Cr). Mean annual 24–h PM_{10} levels varied from 166.5–192.3 µg m^{-3} at the sites (8–10 times of the WHO limit). Weekday/weekend effects on PM_{10} and associated metals were investigated. Significant seasonal variations (ANOVA, p<0.001) in species concentrations were observed with PM_{10} and crustal metals peaking in summer while anthropogenic metals peaked in winter. Spatial distributions of metals were influenced mainly by proximity to traffic and industrial areas. Influence of meteorological parameters on ambient metal distributions was also studied. Source apportionment by principal component analysis–multiple linear regression (PCA–MLR) identified three major sources: crustal (49–65%), vehicular (27–31%) and industrial (4–21%). As a part of health risk assessment, calculated theoretical estimates of blood lead levels in children varied from 10.2–13.3 µg dL^{-1}, indicating some degree of lead toxicity. Incremental lifetime cancer risk (ILCR) assessment showed that up to 2 908 excess cancer cases (102 for Cd, 2 559 for Cr (VI) and 247 for Ni) are likely in Delhi for lifetime inhalation exposure to these species at their current concentrations.

Keywords:
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1. Introduction

It has been estimated that urban air pollution causes ~360 000 premature deaths each year in Asia (Stone et al., 2010) while an estimated 10 500 premature deaths occur per year in Delhi, the capital of India, for the same reason (Gurjar et al., 2010). Over the past decade, a large number of epidemiological studies have established a definite link between airborne particles and human mortality and/or morbidity (Schwartz et al., 1996; Pope and Dockery, 2006). Recent studies have put forth the opinion that chemical composition of particulates, especially the presence of small amounts of toxic chemicals, is a more appropriate parameter for the assessment of particulate health effects rather than their mass concentrations (Forsberg et al., 2005). In this context, metallic species are a class of atmospheric pollutants that are key determinants of the health effects of particulate matter. Some of these metals are known to induce formation of reactive oxygen species (ROS) and hydroxyl radicals (•OH) in biological tissues (de Kok et al., 2006; Nawrot et al., 2009) while others can trigger neurological disorders, different forms of cancer and other ailments (Canfield et al., 2003; IARC, 2009). Effective and cost–efficient regulation of these toxic metals in the atmosphere is not always achieved with a general reduction in aerosol concentrations (von Schneidemesser et al., 2010); proper identification and quan–tification of their sources and a comprehensive assessment of the risks they pose to human health are essential in prioritizing miti–gation requirements.

With these objectives in mind we aimed at characterizing ambient inhalable particles (PM_{10}, aerodynamic diameter ≤10 µm) with respect to 8 major and trace metals (Fe, Mn, Cd, Cu, Ni, Pb, Zn and Cr) at three residential areas of Delhi. Previous studies from this area have generally focused on "pollution hot spots" such as traffic, industrial and commercial sites and, consequently, under–standing of the pollution scenario in typical residential areas of Delhi is fairly weak. Pollution assessment in residential areas is important since outdoor air quality has a major influence on indoor pollution. Population residence time is also highest in residential areas which results in greater exposure. The major sources of atmospheric pollution in Delhi include ~129 000 industrial units located in 31 authorized industrial estates and several non–conforming areas (mostly within the city), three coal–fired power plants (combined capacity ~1 100 MW) and a staggering vehicular population of ~6.6 million. As such, land–use patterns in Delhi are overlapping and essentially mixed, which means that residential areas are likely to be impacted by a host of different sources that needs to be delineated. Overall, this study aims to present a holistic view of the distribution, spatio–temporal variation and source apportionment of metallic species at some residential areas of Delhi along with an estimation of possible health risks to the exposed population.

2. Materials and Methods

2.1. Study area

Delhi (28°37'N, 77°12'E, population 17 million) is spread over an area of 1 483 km^2 with an average elevation of approximately 216 m above sea level. The region is characterized by intensely hot summers (monthly mean temperatures of 32–34 °C in May–June) and cold winters (monthly mean temperatures of 12–14 °C in December–January). The mean annual rainfall is 714 mm, of which

around 80% is received during the monsoon months (July to October). The predominant wind direction is from the north and northwest (Figure 1) except during the monsoon season that is characterized by easterly or southeasterly winds.

2.2. Description of sampling sites

Locations of the sampling sites are shown in Figure 1. Site 1, Rajghat (RG), is located in central Delhi lying 1–2 km northwest of Rajghat and Indraprastha coal–fired power plants and 8–10 km east–southeast of a cluster of industrial areas (Wazirpur, Jahangirpuri, Mangolpuri, Naraina etc.). A traffic intersection is present at a distance of ~800 m. The sampler was located on the roof of a government building at about 8 m from the ground. Site 2, Mayur Vihar (MV), is located 4–4.5 km southeast of Rajghat and Indraprastha power plants and ~600 m away from the Noida Link Road. The sampler was located on the roof of Ahlcon International School at a height of around 12–13 m. The Patparganj Industrial Area is located around ~3 km to the northeast. Site 3, Mithapur (MP), is a suburban residential area located ~2.5 km southeast of Badarpur power plant and 5–7 km southeast of Okhla Industrial Area (Phase I, II and III). The heavy–traffic Delhi–Mathura highway is at a distance of about 1.5 km. The sampler was located on the roof of a private household building at a height of approximately 12 m.

2.3. Sampling protocol

PM_{10} samples were collected simultaneously at the three sites for a period of one year (December 2008–November 2009). The sampling frequency was once a week and sampling duration for each sample was 24 hours (10 AM to 10 AM the following day). Seasonal distribution of samples was as follows: winter –15 each at RG, MV and MP; summer –13 at RG, 16 at MV and 15 at MP; monsoon –15 at RG, 13 at MV and 14 at MP. A number of samples were lost due to logistical problems such as electrical failure, sampler malfunction etc. A total of 131 samples (43 at RG and 44 each at MV and MP) were collected over the course of this study. Around 63% of the sampling days were weekdays (Monday–Friday) while the remaining 37% were weekends (Saturday–Sunday). PM_{10} was trapped on Whatman GF/A (8" × 10") glass fiber filters (precombusted at 450°C for 12 hours) using High–volume samplers (Respirable Dust Sampler, Model MBLRDS–002, Mars Bioanalytical Pvt. Ltd.) having a constant flow rate of 1.2 m^3 min^{-1}. High–volume sampling with glass fiber filters is widely used for atmospheric metal determination (Vijayanand et al., 2008; Shridhar et al., 2010; Paulino et al., 2010; Yatkin and Bayram, 2010). Filters were transported to and from the field in sealed polyethylene bags and were desiccated for 48 hrs before and after use. PM_{10} loads were determined gravimetrically by weighing the filters twice in a microbalance (Model AE163, Mettler, sensitivity 0.0001 g) after proper conditioning. Filters were stored in a refrigerator (4 °C) until analysis.

2.4. Extraction and analysis of metals

Metal extraction was carried out using a microwave digestion system (Speedwave MWS–3^+, Berghof, Germany) consisting of a 2 450 MHz microwave power system with a maximum power of 1 450 W. It houses 12 DAP–100 TFM^{TM} pressure vessels equipped with temperature and pressure sensors, screw caps and rupture discs. The maximum operable temperature and pressure are 230°C and 40 bars, respectively.

Two circular portions (4 cm–diameter each) cut from diagonal locations on each filter paper using a stainless steel punch were digested with a mixed acid solution (10 mL HNO_3 + 3 mL HF) according to the following program: (i) temperature ramped to 150°C within 10 min with a dwell time of 5 min, (ii) a further ramp to 190°C within 5 min with a dwell time of 5 min, (iii) temperature reduced to 100°C within 5 min with a dwell time of 15 min. The pressure was kept at 25 bars. The vessels were allowed to cool for 30 min and were vented and opened in a fume hood. After subse–quent filtration and volume make–up to 25 ml with high–purity deionized water (18.2 MΩ cm^{-1}, Milli–Q system, Millipore, USA), the extracted solutions were transferred to polypropylene bottles and refrigerated until analysis. Metal analysis was carried out using a flame atomic absorption spectrometry system (Solaar M Series, Thermo Scientific) under optimized conditions. Metal recoveries were checked by spiking samples with standard solutions prior to extraction.

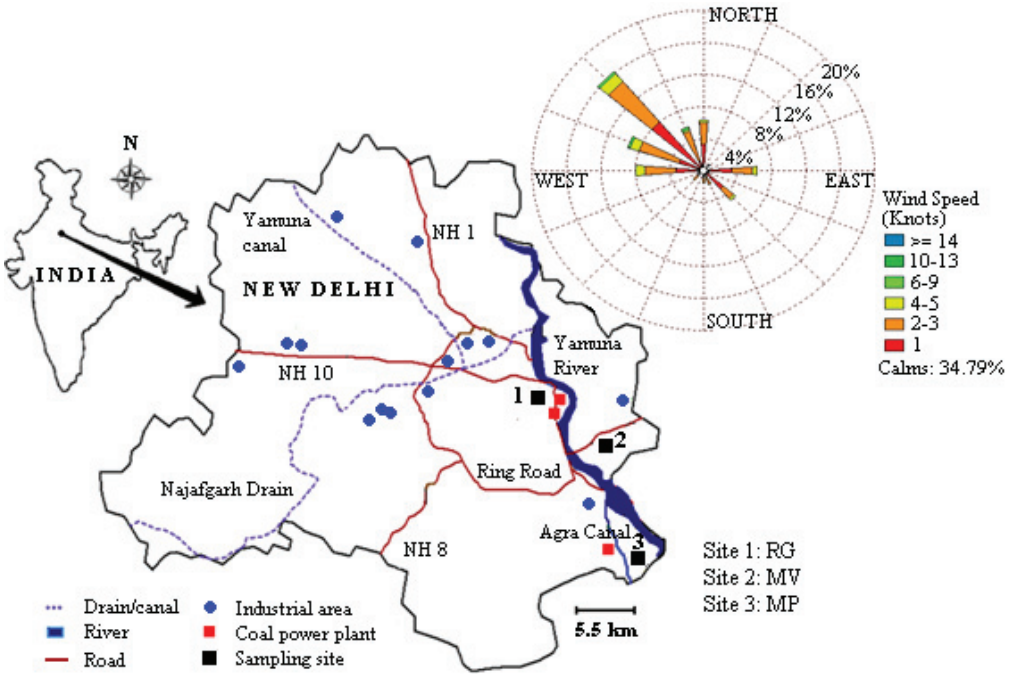

Figure 1. *Map showing the sampling sites and wind rose showing the prevalent wind direction in Delhi during the study period (December 2008 – November 2009).*

2.5. Analytical quality control

The AA spectrometer was calibrated for each metal individually using sets of five standards (Reagecon, Ireland) covering the range of concentrations encountered in ambient air work. The calibration curves were linear in the concentration range with linear regression coefficients (R^2)>0.995 for linear least–squares fit of data. Samples were analyzed in triplicates to ensure precision. Values reported are means of such triplicate analyses. Relative standard deviations (RSDs) of replicate samples were less than 10%. To check homogeneity we separately analyzed three samples (each comprising of two 4 cm–diameter circles located diagonally of each other) taken from different spots on the same filter and found that RSDs for the analyzed metals were <17% in such replicates. Field blanks (around 20% of the total number of samples) and reagent blanks (one for each batch of samples) were analyzed to determine analytical bias. The data were subsequently blank–corrected as required. Detection limits (3σ) of metals were 5.2, 1.4, 0.6, 1.7, 5.4, 8, 0.8 and 3.1 ng m^{-3} for Fe, Mn, Cd, Cu, Ni, Pb, Zn and Cr, respectively. Metal recoveries ranged from 76–97%.

3. Results and Discussion

3.1. PM_{10} mass concentrations

Mean annual PM_{10} at RG, MV and MP were 166.5 ± 54.7, 175.5 ± 67.6 and 192.3 ± 63.4 μg m^{-3}, respectively (Table 1), giving an overall mean of 178.2 ± 62.7 μg m^{-3} for Delhi. These values are ~3 times the annual PM_{10} National Ambient Air Quality Standard (NAAQS) (60 μg m^{-3}) prescribed by the Central Pollution Control Board (CPCB) of India (MoEF, 2009) and around 8–10 times the annual PM_{10} air quality guideline (AQG) (20 μg m^{-3}) set by the World Health Organization (WHO, 2006). The 24–h PM_{10} NAAQS (100 μg m^{-3}) was violated on 88%, 89% and 93% of the sampling days at RG, MV and MP, respectively. The overall mean PM_{10} concentration (mean of three sites) on weekdays (186.4 ± 41.8 μg m^{-3}) was greater than that on weekends (160.9 ± 70.2 μg m^{-3}) but the difference was not statistically significant (independent samples t–test, $t = 1.55$, $p = 0.13$). Assuming industrial and domestic emissions do not show day–of–the–week variations, higher PM_{10} concentrations on weekdays could be attributed to increased traffic. Spatial variations of PM_{10} were not statistically significant ($F = 2.2$, $p = 0.12$, Table 1), which probably suggests that the study sites were impacted by similar sources.

3.2. Loadings and spatial variation of ambient metals

Descriptive statistics of PM_{10}–associated metal concentrations are presented in Table 1. The most abundant metals were Fe and Zn with concentrations in the range of several μg m^{-3} whereas Cd was the least abundant with concentration ranges of several ng m^{-3}. A comparison has been made between the metal concentrations observed in this study and those reported from other parts of India and the world (Singh et al., 2002; Heal et al., 2005; Sanchez de la Campa et al., 2007; Meresova et al., 2008; Vijayanand et al., 2008; Kulshrestha et al., 2009; Jorquera, 2009; Limbeck et al., 2009; Contini et al., 2010; Khan et al., 2010; Shridhar et al., 2010; Theodosi et al., 2010; von Schneidemesser et al., 2010) in Table 2. It is evident that concentrations of inhalable metals in residential areas of Delhi – although comparable, in some cases, with other Indian and Asian cities – are often more than an order of magnitude greater than their European or US counterparts. Metal concentrations obtained in this study were also compared with those observed at an urban background site in Delhi (Jawaharlal Nehru University campus, JNU) for the same time period (Sarkar and Khillare, submitted for publication). JNU is an institutional area in south Delhi situated on a ridge of the Aravalli Hills in the midst of a 4 km^2 forested area. It is widely regarded as a clean and sensitive area of Delhi (Srivastava and Jain, 2008). Nearest traffic and industrial areas are at least 2 km and 8–9 km away, respectively. Concentrations of PM_{10} and a majority of the metals at JNU were found to be lower than RG, MV and MP by the following amounts: PM_{10} (28–37%), Fe (3–30%), Cd (50–79%), Pb (41–65%), Zn (24–34%) and Cr (46–70%). Manganese, copper and nickel concentrations at JNU were more or less comparable with those at RG, MV and MP. Overall, it was observed that concentrations of PM_{10} and a number of metals at the chosen residential areas of Delhi were distinctly higher than those at the urban background site.

Inter–site variations were significant for all metals except Zn ($F = 1.8$, $p = 0.2$). Absence of significant spatial variations in Zn concentration probably indicates ubiquitous traffic sources near the sampling sites. In fact, Cu/Zn ratios at RG, MV and MP were 0.04 ± 0.04, 0.07 ± 0.04 and 0.06 ± 0.05, respectively, all of which strongly suggest vehicular sources (Cadle et al., 1999). Spatial variations were in general more pronounced for anthropogenic metals than their crustal counterparts. Concentrations of Cd, Ni and Pb at MP were significantly higher (p<0.05) than RG. Proximity to a major coal–fired power plant and an industrial area could be the reasons for higher metal concentrations at MP. Being a suburban residential area, domestic emissions (in the form of charcoal, biomass and low–grade coal combustion) could also be significant. In comparison, RG is a relatively cleaner site lying upwind of power plants and having fewer emission sources in the vicinity. Comparatively lower concentrations of anthropogenic metals at this site are hence expected. The other site, MV, exhibited metal concentrations that were in many cases intermediate between and not significantly different from those at RG and MP. Overall, we noted that the differences in metal concentrations between the three investigated sites, although statistically significant in most cases, were not extremely high. This is expected to some extent because all three sites were typically residential in nature with similar land–use patterns and were possibly impacted by similar sources. Concentrations of traffic tracers (Cu, Zn and Cr) were on an average 3–14% higher on

Table 1. *Seasonal and spatial distribution of ambient PM_{10} and associated metals (μg m^{-3}). Also shown are the results of two–way ANOVA test (F–values along with corresponding significance levels)*

	RG			MV			MP			RG (N = 43)	MV (N = 44)	MP (N = 44)	*F*–values two–way ANOVA		
Species	**W**	**S**	**M**	**W**	**S**	**M**	**W**	**S**	**M**	**Mean ± SD**	**Mean ± SD**	**Mean ± SD**	**Season**	**Site**	**Season*Site**
PM_{10}	165.1	205.8	133.8	184.7	210.3	122	194.9	215.9	164.2	166.5 ± 54.7	175.5 ± 67.6	192.3 ± 63.4	17.2^{c}	2.2^{NS}	0.6^{NS}
Fe	7	12.1	5.5	9	12.4	6.7	10.5	13	10	8 ± 3.7	9.6 ± 4.4	11.2 ± 4.3	23.2^{c}	7.7^{b}	1.2^{NS}
Mn	0.34	0.37	0.26	0.27	0.37	0.21	0.22	0.32	0.2	0.32 ± 0.1	0.29 ± 0.1	0.25 ± 0.1	14.2^{c}	4.5^{a}	0.7^{NS}
Cd	0.014	0.005	0.005	0.022	0.014	0.011	0.028	0.018	0.011	0.008 ± 0.006	0.016 ± 0.01	0.019 ± 0.015	19.2^{c}	16.1^{c}	0.7^{NS}
Cu	0.28	0.16	0.08	0.25	0.34	0.22	0.26	0.21	0.16	0.18 ± 0.1	0.27 ± 0.1	0.21 ± 0.1	12.3^{c}	8.6^{c}	4.5^{b}
Ni	0.44	0.32	0.15	0.39	0.3	0.13	0.46	0.39	0.25	0.3 ± 0.2	0.28 ± 0.2	0.37 ± 0.2	49^{c}	7^{c}	0.5^{NS}
Pb	0.41	0.24	0.14	0.47	0.49	0.25	0.51	0.54	0.33	0.27 ± 0.2	0.41 ± 0.2	0.46 ± 0.3	17.8^{c}	13.3^{c}	1.5^{NS}
Zn	4.4	4.4	5.3	5.3	4.7	2.7	5.7	4	2.6	4.7 ± 1.7	4.3 ± 1.5	4.1 ± 2.1	11.7^{c}	1.8^{NS}	8^{c}
Cr	0.17	0.17	0.07	0.32	0.17	0.09	0.32	0.27	0.09	0.13 ± 0.07	0.2 ± 0.12	0.23 ± 0.18	36.3^{c}	8.7^{c}	3.2^{b}

W, S and M denote winter (November – February), summer (March – June) and monsoon (July – October) seasons, respectively; Mean ± SD refers to the annual mean values ± one standard deviation at the sites; N denotes the number of samples collected at a particular site; Level of significance: ^{NS}not significant, ^{a} p<0.05, ^{b} p<0.01, ^{c} p<0.001.

Table 2. *Comparison of ambient metal concentrations (μg m^{-3}) observed in the present study with those from other parts of India and the world*

Location/Site type/ PM type	Fe	Mn	Cd	Cu	Ni	Pb	Zn	Cr	Reference
Delhi, India/R/PM_{10}	8–11.2	0.25–0.32	0.01–0.02	0.18–0.27	0.28–0.37	0.27–0.46	4.1–4.7	0.13–0.23	Present study
Coimbatore, India/R/SPM	2.9–6	NR	BDL	0.7–0.77	0.16–0.22	0.21–0.62	11.3–20.7	0.005–0.88	Vijayanand et al., (2008)
Agra, India/U/PM_{10}	2.9	0.9	NR	0.1	0.2	1.1	0.5	0.3	Kulshrestha et al., (2009)
Delhi, India/U/SPM	16.4	0.74	0.01	3.7	0.15	0.44	4.7	0.35	Shridhar et al., (2010)
Lahore, Pakistan/U/PM_{10}	8.2	0.3	0.08	0.07	0.02	4.4	11	0.03	von Schneidemesser et al., (2010)
Beijing, China/R/PM_{10}	4.6	0.21	0.005	0.09	0.01	0.33	0.64	0.02	Khan et al., (2010)
Tocopilla, Chile/R/PM_{10}	3.5	0.06	NR	1.1	0.0009	0.01	0.01	NR	Jorquera, (2009)[a]
Istanbul, Turkey/U/PM_{10}	0.7	0.02	0.001	0.02	0.007	0.07	0.24	0.004	Theodosi et al., (2010)
Lecce, Italy/UB/PM_{10}	0.31	0.008	NR	0.01	0.003	0.008	0.03	0.002	Contini et al., (2010)
Vienna, Austria/U/PM_{10}	0.78	0.01	0.0005	0.02	0.006	0.01	0.04	0.006	Limbeck et al., (2009)
Bratislava, Slovakia/U/NR	0.25	0.005	0.0001	0.008	0.0005	0.02	0.03	0.001	Meresova et al., (2008)
Huelva, Spain/U/PM_{10}	0.7	0.01	0.0006	0.05	0.004	0.02	0.03	0.003	Sanchez de la Campa et al., (2007)
Edinburgh, UK/UB/PM_{10}	0.18	0.003	0.0003	0.005	0.003	0.01	0.01	0.002	Heal et al., (2005)[b]
Los Angeles, USA/U/PM_{10}	0.15	0.002	NR	0.003	0.0006	0.002	0.004	0.001	Singh et al., (2002)

R: residential site, U: urban site, UB: urban background site; NR: not reported; BDL: below detection limit

[a] *sampling in March–April 2006*

[b] *median values*

weekdays as compared to weekends, but the differences were not statistically significant (p>0.05). This possibly suggests that traffic volumes were not significantly different at the sites between weekdays and weekends.

3.3. Enrichment Factors of metals

Enrichment Factors (*EF*s) of metals were calculated as $EF = (X_{aerosol}/Ref_{aerosol})/(X_{UCC}/Ref_{UCC})$ where X is the element under consideration both in aerosol and the upper continental crust (UCC), and *Ref* is a reference element that is typically crustal such as Al, Fe, Li, Ti etc. Metal abundances in UCC given in Wedepohl (1995) were used and Fe was chosen as the reference metal. Three distinct groups existed among the metals on the basis of their EFs. Manganese was non–enriched in aerosol with mean *EF*s of 2.6 ± 1.1, 2 ± 0.9 and 1.4 ± 0.7 at RG, MV and MP, respectively. Manganese is typically dominated by crustal contributions, the form found in soil largely being MnO_2 (von Schneidemesser et al., 2010). A second group of elements comprising of Cr (16.5 ± 14.6 – 20.6 ± 13.9), Cu (46.4 ± 28.4 – 68.5 ± 38), Ni (56 ± 36.9 – 71.6 ± 50.2) and Pb (67.8 ± 49.3 – 83.9 ± 39.6) had *EF*s between 10–100 and were moderately–enriched. This is in agreement with published literature as all the elements belonging to this group have a known crustal source in addition to various emission sources (Salvador et al., 2004; Khan et al., 2010). The third group represented by Zn (244.9 ± 155 – 418.3 ± 243) and Cd (386.1 ± 409.8 – 595.3 ± 397.5) had extremely high *EF* values (between 100–1 000) and were anomalously enriched in aerosol. Vehicular tire wear, battery–manufacture, pigments, metal plating and smelting industries are important sources of these metals (Birmili et al., 2006; Querol et al., 2007).

3.4. Seasonal variation of PM_{10}, metals and influence of meteorological parameters

Table 1 shows the seasonal variations of PM_{10} and associated metals at the study sites. Meteorological parameters recorded in Delhi during the sampling period and the results of correlation analysis between species concentrations and meteorological parameters are provided in Supporting Material (SM) (Tables S1 and S2, respectively). Considering an average aerosol residence time of 5 days, we divided the meteorological data into sets of 5 days (prior to and including the sampling date) to take into account the atmospheric conditions that may have helped in the build–up (or loss) of metal concentrations over a period of time culminating on the sampling date.

Overall, seasonal variations of PM_{10} and ambient metals were highly significant (ANOVA, p<0.001, Table 1), which shows that seasonal conditions possibly influence both the source strengths and the atmospheric accumulation of these species. Levels of PM_{10} and metals such as Fe and Mn showed a clear seasonal trend of summer>winter>monsoon with significantly higher concentrations in summer as compared to the other seasons (ANOVA with multiple comparisons, p<0.01). The summer season is generally characterized by a high degree of crustal resuspension (of coarser particles) that leads to higher levels of PM_{10} and crustal metals. Dust storms ("Andhi") are common in Delhi during summer that carry large amounts of suspended particulate matter (as high as 500–800 tonnes $mile^{-2}$) from the Thar Desert into Delhi (Singh et al., 2008). Mean temperature, wind speed and the number of bright sunshine hours were positively correlated with the crustal metal Fe (p<0.01, see the SM, Table S2), which is because high solar radiation during summer induces atmospheric convection favoring crustal resuspension and strong winds favor atmospheric dust transport (Querol et al., 2002). Metals such as Cd, Ni, Zn and Cr, on the other hand, had significantly higher concentrations in winter (multiple comparisons, p<0.05) and were negatively correlated with temperature, wind speed and the number of bright sunshine hours. These metals have important anthropogenic sources such as metal smelting (Zn), battery manufacture (Cd, Ni), oil combustion (Ni) (Pacyna and Pacyna, 2001) and vehicular emissions (tailpipe/abrasion) (Zn, Cd, Cr) (Lin et al., 2005; Birmili et al., 2006). Emissions from these sources are trapped and stabilized under inversion layers in winter, leading to higher abundances in ambient aerosol. Relative humidity had significant negative correlations with crustal metals (r = –0.56, –0.53 with Fe and Mn, respectively, p<0.001), which shows that atmospheric moisture enhances settling of suspended particles and prevents crustal resuspension by wetting of soil particles. Understandably, rainfall was negatively correlated with almost all metals as precipitation scavenging is an important mechanism of particulate–removal from the atmosphere (Seinfeld and Pandis, 2006).

3.5. Source apportionment of ambient metals

Principal component analysis coupled with multiple linear regression (PCA–MLR) (SPSS 14.0) was used to identify and quantify sources of atmospheric metals. The multiple linear model used here is the one described in Larsen and Baker (2003)

$$y = \sum m_i X_i + b \quad (1)$$

where PCA factor scores serve as the independent variables (X_i) and the total metal concentration in aerosol serves as the dependent variable (y). The influence of each independent variable on the dependent variable can be directly compared by the regression coefficients, if the dependent and independent variables are normally standardized. When the variables of Equation (1) are normalized, the regression coefficients are

represented as *B*, and the intercept (*b*) is zero. The equation becomes:

$$z = \sum B_i X_i \quad (2)$$

where *z* is the standardized normal deviate of the total metal concentration in aerosol (the dependent variable), B_i is the partial regression coefficient and X_i is the PCA factor score for source *i* (the independent variable). By expanding *z* and rearranging terms, we get the following multiple linear regression equation:

$$TM = \sum B_i \sigma_{TM} FS_i + TM^* \quad (3)$$

where *TM* is the total metal concentration in aerosol, TM^* is the mean total metal concentration, σ_{TM} is the corresponding standard deviation and FS_i is the factor score for source *i*. The mean contribution of source *i* can then be calculated as:

$$mean\ contribution\ of\ source\ i\ (\%) = 100\left(\frac{B_i}{\Sigma B_i}\right) \quad (4)$$

and daily contributions can be calculated as:

$$daily\ contribution\ of\ source\ i\ (\mu g\ m^{-3}) = TM^*\left(\frac{B_i}{\Sigma B_i}\right) + B_i \sigma_{TM} FS_i \quad (5)$$

where $B_i/\Sigma B_i$ is the ratio of the regression coefficient for factor *i* to the sum of all the regression coefficients.

PCA factors were identified using Varimax rotation with Kaiser Normalization. Eigenvalue>1 was the criterion for selecting factors and a factor score of 0.5 was selected as the lowest level of signif–icance within a factor. PCA factor scores for individual sites are presented in Table 3.

Three factors explained 78.4% variance of the data at RG. The first factor (PC1) was loaded with Cd, Cu, Ni and Pb representing impacts of industrial sources present in the upwind direction (possibly in the form of metal smelting, metal product manufacture and industrial oil combustion) (Querol et al., 2007; Kulshrestha et al., 2009). PC2 was dominated by Fe, Mn and Cr suggesting crustal origin (Shridhar et al., 2010). PC3 was dominated by Zn and moderately loaded with Mn. Zinc is a known tracer of tire wear particles (Birmili et al., 2006; Wang et al., 2006). Manganese was predominantly crustal in this study (see Section 3.3) indicating that its loading in this factor was probably due to resuspension of road dust by vehicular turbulence. So, this factor represents vehicular sources.

Three factors were identified that explained 75.5% data variance at MV. PC1 was loaded with Cd, Ni, Pb, Zn and Cr, possibly indicating industrial emission sources (Querol et al., 2007; Kulshrestha et al., 2009) from the Patparganj Industrial Estate. PC2 was highly loaded with Mn, Cd and Cu, and to a lesser extent with Fe, denoting vehicular resuspension of road dust and brake–drum abrasion particles (Birmili et al., 2006; Wang et al., 2006). PC3 was loaded with Fe and Pb indicating resuspension of crustal and road–dust possibly containing residual Pb–additives.

Three factors explained 74.1% variance of the dataset at MP. PC1 was significantly loaded Cd, Ni, Zn and Cr, suggesting industrial emissions possibly originating from the Okhla Industrial Area present upwind of the site. PC2 was dominated by Cu, Pb and Cr suggesting emissions from brake–drum abrasion (Wang et al., 2006) and resuspension of road dust by vehicular turbulence. PC3 had high loadings of Fe and Mn indicating a crustal source.

Observed and PCA–MLR–predicted total metal concentrations agreed strongly ($0.80<R^2<0.87$, Figure 2), which shows that variations in observed metal concentrations are well explained by the sources apportioned by PCA–MLR. Figure 2 also shows the mean annual contributions of apportioned sources to total metal concentrations at the sites along with the time–evolution of the corresponding source contributions. Crustal sources dominated with 49–65% contribution to ambient metals on a mass basis. As preparations for the Commonwealth Games 2010, Delhi Government took up 59 projects/schemes (mostly construction–related) all over the city (Planning Department, 2009), including construction of the Commonwealth Games Village on the east bank of Yamuna (~2 km northwest of MV), renovation of the Indira Gandhi Indoor Stadium (~1 km south of RG) and construction of a flyover at the Delhi–Faridabad border (~1.5 km northwest of MP). These might have served as local sources of crustal matter at the sites. In fact, spatial variation in the crustal source contributions was not significant (ANOVA, $F = 1.06$, $p = 0.35$) showing that the sites were similarly affected by this source. On the other hand, its seasonal variation was highly significant (ANOVA, $F = 27.2$, $p<0.001$) with distinctly higher contributions in summer. Summer–time migration of trans–boundary dust carried by strong westerly and northwesterly winds might be an important factor contributing to this source.

Vehicular sources contributed 27–31% at the sites with insignificant spatial ($F = 3.1$, $p = 0.05$) and seasonal ($F = 1.5$, $p = 0.22$) variations. This shows that traffic was nearly ubiquitous at all the sites and the nearness of these sites to traffic precluded the importance of atmospheric conditions on the transport of traffic–generated metals to the sites. Delhi's vehicular population has grown at a decennial rate of 85.5% between 1997–98 and 2007–08 and private car penetration in the city (85 cars/1 000 population) is more than 10 times the national average (8 cars/1 000 population)

Table 3. *Results of Principal Component Analysis (varimax rotation with Kaiser Normalization) at the individual sites. Only factor loadings ≥0.3 are shown. Loadings ≥0.5 are in bold*

	RG			MV			MP		
	Principal Components			Principal Components			Principal Components		
Species	**PC1**	**PC2**	**PC3**	**PC1**	**PC2**	**PC3**	**PC1**	**PC2**	**PC3**
Fe		**0.92**			0.36	**0.79**		0.30	**0.86**
Mn		**0.67**	0.43		**0.82**				**0.84**
Cd	**0.88**			**0.54**	**0.60**		**0.82**		
Cu	**0.85**				**0.77**		0.43	**0.65**	
Ni	**0.81**	0.35		**0.80**			**0.71**		
Pb	**0.86**			**0.52**		**0.70**		**0.88**	0.36
Zn			**0.94**	**0.82**		0.33	**0.80**	0.30	
Cr	0.39	**0.67**		**0.91**			**0.57**	**0.64**	
Eigenvalues	3.13	2	1.13	2.71	1.83	1.51	2.38	1.9	1.65
% of variance	39.14	25.11	14.11	33.82	22.83	18.89	29.7	23.74	20.65
Cumulative %	39.14	64.25	78.35	33.82	56.65	75.54	29.7	53.45	74.1

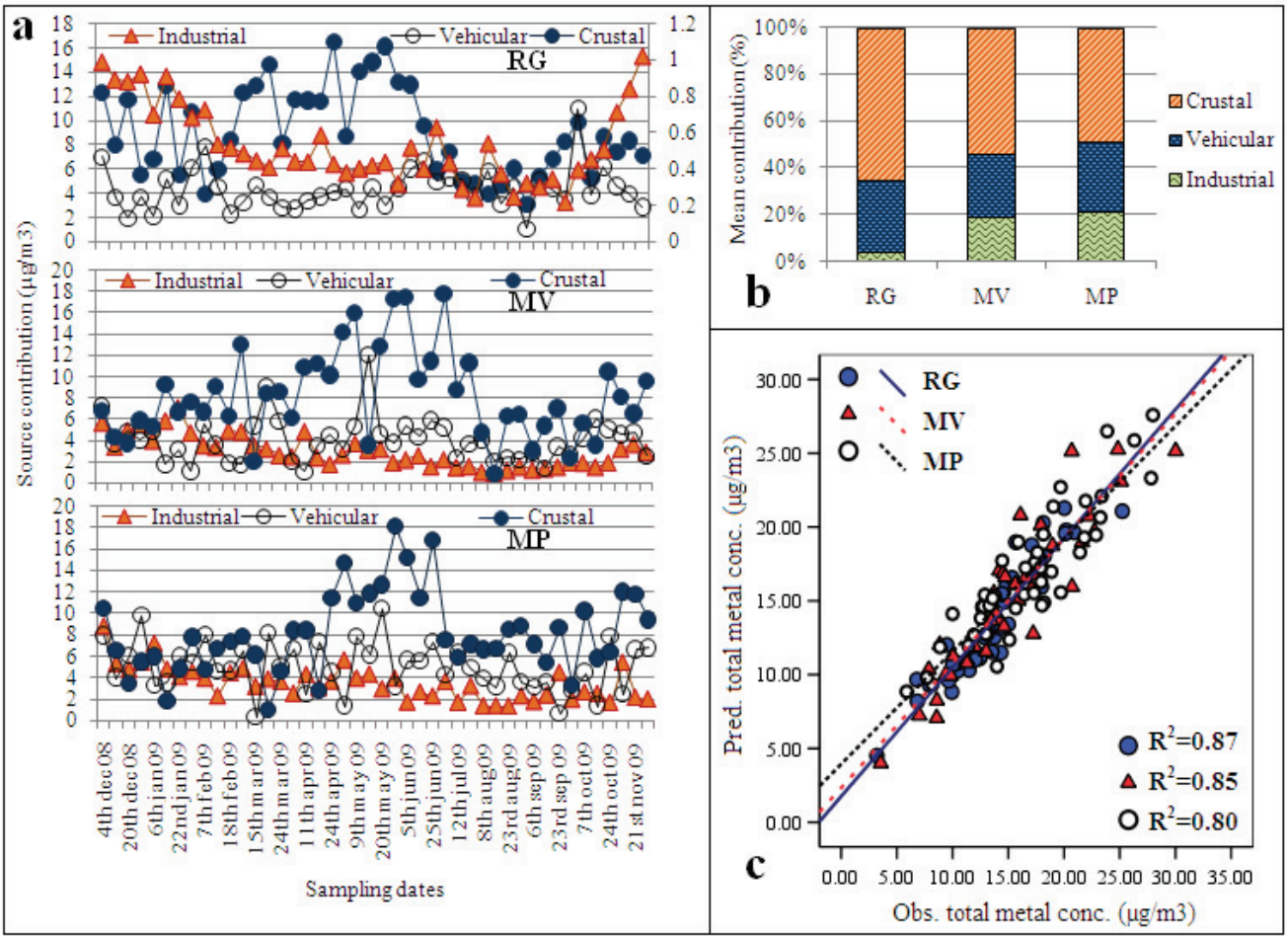

Figure 2. *Time–evolution of source contributions (µg m^{-3}) at the study sites **(a)**; mean annual contribution of apportioned sources at the study sites **(b)**; agreements between observed and model–predicted total metal concentrations at the sites **(c)**.*

(Planning Department, 2009). With this trend continuing, the vehicular source could become even more important in the coming years. Industrial emissions accounted for 4–21% of the analyzed metal mass and showed significant spatial (F = 116.8, p<0.001) and seasonal variation (F = 39.1, p<0.001). The moderate distance of these sites from the nearest industrial areas (3–10 km) required that the emitted pollutants be atmospherically transported from the source to the receptor, thus depending heavily on seasonal variations in atmospheric conditions. Most of the small–scale industries located in Delhi cannot afford pollution abatement technologies and pose severe problems for effective monitoring and enforcement.

3.6. Potential health risks to the exposed population

Theoretical estimates of blood lead levels in children. Ambient Pb concentrations (0.27 ± 0.2, 0.41 ± 0.2 and 0.46 ± 0.3 µg m^{-3} at RG, MV and MP, respectively) were lower the NAAQS (0.5 µg m^{-3}, annual average). Airborne Pb concentrations in India have declined significantly since the complete phase–out of leaded gasoline in 1999; however, the levels found in this study are still higher than many other cities (Table 2).

The relationship between blood lead (PbB) of children and air lead (PbA) can only be weakly estimated because of a number of factors (Brunekreef, 1984): firstly, since children spend only a small fraction of their time outdoors, Pb concentration measured in outdoor air is poorly correlated to personal Pb exposure; secondly, PbB shows large variability near lead emitting sources such as smelters whereas in urban areas the variability is much less; lastly, environmental factors varying between studies also influences the relationship to a large extent. Despite this variability, Brunekreef (1984) compiled data from 96 different child populations of varying ages, from different countries, from 18 different study areas and found a statistically significant relationship between PbB and PbA as ln PbB = 2.8528 + 0.3485 ln PbA (R^2 = 0.692 after log–transformation). This relationship may tend to overestimate PbB at high levels of exposure and upon restricting the analysis to populations with PbB<20 µg dL^{-1} (N = 43), a second relationship was suggested as a more conservative estimate in the form of ln PbB = 2.607 + 0.2159 ln PbA (R^2 = 0.331) (Brunekreef, 1984; Browne et al., 1999). We used these two equations as upper and lower estimates, respectively, and found estimated PbB in children living near RG, MV and MP sites to be 10.2–10.9, 11.2–12.7 and 11.5–13.3 µg dL^{-1}, respectively. We also compared these estimates with actual PbB data of children reported by various authors from India (specifically, from Delhi, Mumbai and Chennai) to check the applicability of the equations in the Indian scenario. Jain and Hu (2006) studied PbB levels in 1 081 children belonging to Mumbai and Delhi and found that most of the children (76%) had PbB values between 5 and 20 µg dL^{-1}. Kalra et al., (2003) studied PbB levels of 190 children (125 school children and 65 children belonging to an urban slum) in Delhi and found a mean value of 7.8 ± 3.9 µg dL^{-1} while Roy et al., (2009) found a mean PbB level of 11.4 ± 5.3 µg dL^{-1} among 756 children in Chennai. It is apparent that our estimates agree very well with the actual PbB data reported by these authors, which means that the representativeness of the equations in the present case is well–justified. The United States Center for Disease Control (CDC) defines elevated blood lead levels as ≥10 µg dL^{-1} (CDC, 1991) and recommends that children with blood lead ≥20 µg dL^{-1} should be referred for medical evaluation. However, adverse health effects have been observed

for concentrations below 10 μg dL^{-1} (Canfield et al., 2003). For example, Roy et al., (2009) found that a mean PbB level of 11.4 ± 5.3 μg dL^{-1} in children of Chennai was associated with higher anxiety, social problems and greater attention–deficit hyperactivity disorder (ADHD). Our estimates are quite comparable to these values and it seems that children living in the study areas might suffer from some degree of lead toxicity.

Incremental lifetime cancer risk assessment. The overall annual averages of Ni and Cd in this study (316 ± 161 and 14 ± 12 ng m^{-3}, respectively) were around 15 and 3 times higher than the stipulated standards (NAAQS for Ni: 20 ng m^{-3} and the European Union target for Cd: 5 ng m^{-3}, EU Directive 2004/107/CE). As per US EPA's weight–of–evidence, Ni is classified as a Group A pollutant (known human carcinogen) while Cd is classified as a Group B1 pollutant (probable human carcinogen) (IRIS, 1995). Hexavalent Cr – unregulated in outdoor air – is also carcinogenic to humans and is classified as a Group A pollutant (IRIS, 1995).

Incremental lifetime cancer risk (ILCR) is the incremental probability of an individual developing cancer over a lifetime (70 years) as a result of exposure to a potential carcinogen. ILCR was calculated based on the method described by Gurjar and Mohan (2003):

$$ILCR = CDI \times ISF \quad (6)$$

where, *CDI* is the chronic daily intake (mg kg^{-1} day) and *ISF* is the inhalation slope factor (mg kg^{-1} $day)^{-1}$.

CDI can be further calculated as:

$$CDI = \frac{(CC \times IR \times EF \times ED \times AF)}{(BW \times LT)} \quad (7)$$

where, *CC* is the contaminant concentration (mg m^{-3}), *IR* is the inhalation rate (m^3 day^{-1}), *EF* is the exposure frequency (days yr^{-1}), *ED* is the exposure duration (yr), *AF* is the absorption fraction, *BW* is the body weight (kg), and *LT* is the average lifetime (days) i.e. age (yr) × 365 days yr^{-1}.

The parameters used in the calculation of ILCR and results of the assessment are presented in Table 4. Concentration of Cr (VI) was assumed to be no less than one–seventh of total Cr (Mancuso, 1975). This serves as a conservative estimate of Cr (VI) and has been used by various recent studies involving risk characterization (Pratt et al., 2000; Gurjar and Mohan, 2003; DEP, 2009). Calculated ILCRs for Cd, Cr (VI) and Ni were 6×10^{-6}, 1.5×10^{-4} and 1.5×10^{-5}, respectively. An ILCR between 10^{-6} and 10^{-4} is generally considered to indicate potential risk while ILCR greater than 10^{-4} suggests high potential health risk. In comparison, the risks estimated in this study are somewhat higher for Cr (VI) and Ni. Societal ILCR was calculated assuming Delhi's population to be 17 million and it was found that up to 2 908 excess cancer cases (102 for Cd, 2 559 for Cr (VI) and 247 for Ni) are possible in Delhi considering lifetime inhalation exposure to these pollutants at their current concen–trations.

4. Conclusion

Eight major and trace metals associated with PM_{10} were characterized at three residential areas in Delhi, India to identify and quantify their major sources. PCA–MLR identified dominance of a crustal source (49–65%) having significantly higher contributions in summer. Local sources such as construction activities, road dust resuspension etc. coupled with trans–boundary migration of dust most likely contributed to this factor. Given the impossibility to control this source, the only viable option left is to prevent resuspension of dust to any feasible degree. Various developed countries have successfully used measures such as large–scale water flushing and chemical suppression to prevent resuspension of road dust (Amato et al., 2010). However, the practical aspects of using such methods in India are yet to be looked into. Vehicular sources contributed 27–31% to ambient metals and included tailpipe/abrasion emissions along with resuspended dust. This source is likely to be even more significant in the finer fraction of ambient particles ($PM_{2.5}$ and less). Industrial emissions (metal smelting and manufacture, oil combustion etc.) contributed 4–21% at the sites. Overall, it was found that residential areas of Delhi are significantly more polluted than their counterparts in other countries. Possible health risks include high estimated blood lead levels (10.2–13.3 μg dL^{-1}) in children and around 2 908 excess cancer cases (102 for Cd, 2 559 for Cr (VI) and 247 for Ni) that are likely in Delhi considering lifetime inhalation exposure to these pollutants at their observed concentrations.

Table 4. *Incremental lifetime cancer risk (ILCR) assessment for exposure to airborne Cd, Cr (VI) and Ni at their respective mean annual concentrations observed in this study*

Species	Concentration	ISF[b]	CDI[c]	ILCR	Societal ILCR[e]
	(mg m^{-3})	(mg kg^{-1} $day)^{-1}$	(mg kg^{-1} day)	(10^{-6})	
Cd	$1.44*10^{-5}$	6.1	$9.86*10^{-7}$	6	102
Cr (VI)[a]	$2.68*10^{-5}$	41	$3.67*10^{-6}$	151	2 559
Ni	$3.16*10^{-4}$	0.84	$1.73*10^{-5}$	15	247
			Total	**198**	**2 908**

[a] *Concentration of Cr (VI) has been calculated as 1/7 of total chromium (Mancuso, 1975).*
[b] *Inhalation slope factor (Source: The Risk Assessment Information System; http://rais.ornl.gov)*
[c] *Chronic daily intake; parameters used for calculating CDI are: Species concentration (mg m^{-3}), Inhalation rate (IR) = 20 m^3 day^{-1}, Exposure frequency (EF) = 350 days yr^{-1}, Exposure duration (ED) = 70 yrs, Absorption fraction = 0.25 for Cd[d], 0.5 for Cr (VI)[d] and 0.2 for Ni[d], Body weight (BW) = 70 kg, Average lifetime (LT) = 70 yrs × 365 days i.e. 25 550 days.*
[d] *Gurjar and Mohan (2003).*
[e] *Societal ILCR = ILCR (10^{-6}) × population (10^6).*

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Supporting Material Available

Meteorological parameters recorded in Delhi during the study period (Table S1), Correlation coefficients observed between analyzed metal concentrations and 5–day averaged meteorological parameters (Table S2). This information is available free of charge via the Internet at http://www.atmospolres.com.

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